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(54) PROCEDE PERMETTANT D'ELIMINER LES IONS DE NICKEL ET DE PLOMB DE SOLUTIONS DE SELS FERREUX
(54) METHOD FOR ELIMINATING NICKEL IONS AND LEAD IONS FROM FERROUS SALT SOLUTIONS

(57)
For purifying an iron(II) salt solution contaminated with nickel ions and lead ions, the hyperstoichiometric addition of sodium sulfide or sodium hydrogen sulfide in the acid range has proved itself as suitable when a residence time in the order of one hour is adhered to before the sulfides are removed by filtration. The residual contents are equal to less than 30 mg per liter for nickel and less than 7.5 mg per liter for lead.

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(54) Titre : PROCEDE PERMETTANT D'ELIMINER LES IONS DE NICKEL ET DE PLOMB DE SOLUTIONS DE SELS FERREUX

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(57) Abrégé/Abstract:
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Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: METHOD FOR ELIMINATING NICKEL IONS AND LEAD IONS FROM FERROUS SALT SOLUTIONS

(54) Bezeichnung: VERFAHREN ZUM ENTFERNEN VON NICKEL- UND BLEIIONEN AUS EISENSALZLÖSUNGEN

(57) Abstract: For purifying an iron(II) salt solution contaminated with nickel ions and lead ions, the hyperstoichiometric addition of sodium sulfide or sodium hydrogen sulfide in the acid range has proved itself as suitable when a residence time in the order of one hour is adhered to before the sulfides are removed by filtration. The residual contents are equal to less than 30 mg per liter for nickel and less than 7.5 mg per liter for lead.

(57) Zusammenfassung: Zur Reinigung einer mit Nickel- und Bleiionen belasteten Eisen(II)salzlösung hat sich die überstöchiometrische Zugabe von Natriumsulfid oder Natriumhydrogensulfid im sauren Bereich als geeignet erwiesen, wenn vor der Abfiltration der Sulfide eine Verweilzeit in der Größenordnung einer Stunde eingehalten wird. Die Restgehalten liegen dann für Nickel unter 30 mg pro Liter und bei Blei unter 7,5 mg pro Liter.

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Process for eliminating nickel and lead ions from iron salt solutions

The invention relates to a method for eliminating nickel and lead ions from iron(II) salt solutions by precipitating and separating the corresponding sulphides.

Heavy-metal ion concentrations in solutions are generally reduced (purification) by chemical precipitation of the corresponding hydroxides or carbonates. On the industrial scale, however, the purification effect expected on the basis of the low solubility product is often not achieved for a variety of reasons. The influencing factors are the time (incompleteness of the reaction), the content of other substances present in the solution (their "ionic strength"), possible complex-forming reactions (conversion into compounds of higher solubility) and, above all, the handling properties of the precipitates (e.g. their filterability).

The precipitation of heavy-metal ions in the form of heavy-metal sulphides is generally also possible, and sometimes also preferred, since the solubility of the sulphides is often sufficiently low even in the acidic range (see, for example, B. D. Bhattacharyya et al., Precipitation of heavy metals with sodium sulfide: Bench-scale and full-scale experimental results, American Institute of Chemical Engineers Symposium Series 209, Vol. 77 (1981) 31-38). However, it is pointed out in L. Bauch et al., Elimination von Blei und Nickel aus salzreichen Wässern durch Sulfidfällung und Flockung [Elimination of lead and nickel from salt-rich waters by sulphide precipitation and flocculation], Vom Wasser, 75, 375-392 (1990) that the low residual concentrations to be expected on the basis of the thermodynamic data are virtually unattainable, particularly for nickel in salt-rich waste water.

The object of the invention was an industrial-scale method for the extensive elimination of lead and nickel ions from iron salt solutions, where the iron ions are predominantly in bivalent state. In this context, "extensive" is taken to mean that a value below 30 mg per litre is reliably achieved for nickel and below 7.5 mg per litre for lead, but that as little dissolved iron as possible is precipitated at the same time.

The object is solved by a method for the elimination of nickel and lead ions from iron(II) solutions by precipitation and separation of the corresponding sulphides, characterised in that an alkali sulphide is added at a super-stoichiometric rate in the acidic range and the precipitate filtered off after a residence time.

Contrary to previous experience, it is possible in this way to purify iron(II) salt solutions economically and reliably on an industrial scale. Nickel ion contents of below 30 mg/l are also achieved in saturated iron(II) solutions. In Germany, for example, these values are prescribed by law for the use of iron(II) salt solutions in water treatment.

The method according to the invention cannot be applied to relatively "pure" aqueous solutions with a low lead and nickel ion content. A sufficiently high content of iron(II) ions, up to the point of saturation, is required for the method, this being the case when using industrial solutions such as those obtained when pickling steel or leaching the cyclone dust occurring when manufacturing titanium dioxide by the chloride process.

Industrial iron(II) salt solutions of this kind always contain iron(III) ions - though often at a low level. They are precipitated sooner than the iron(II) ions, even in the acidic range, and appear to act as "sulphide carriers" for dissolved nickel in a reaction chain. This (slowly formed) Ni_2S_3 (with an extremely low solubility product) is removed from the solution, and this slowness of the reaction is probably the reason for the very long residence time in the region of one hour, which is absolutely essential.

Particularly suitable as precipitants are aqueous solutions of sodium hydrogensulphide or sodium sulphide. As a result of the high iron concentration, no hydrogen sulphide is released under the conditions of the reaction.
An example of the invention is described below.
A typical "contaminated" iron(II) chloride solution of cyclone dust, such as that occurring in the production of titanium dioxide by the chloride process, has the following composition: 8.8% by weight Fe, 1.61% by weight Mn, 2.6% by weight HCl, 410 ppm Ti, 1170 ppm Cr, 2420 ppm V, 580 ppm Nb, 1146 ppm Zr, 95 ppm Ni, 16 ppm Pb. Selective precipitation with a limestone powder suspension (such as described in DE 42 43 559 A1) at a pH value in the region of 3 precipitates the trivalent heavy metals and those of higher valence, especially chromium, vanadium, titanium and zirconium in the form of hydroxides that are filtered off. The heavy-metal ions not affected by hydroxide precipitation and remaining in solution encompass the entire nickel and lead of the original solution, meaning that a solution pre-purified in accordance with DE 42 43 959 A1 exceeds the limit values prescribed by law.

According to the invention, the necessary reduction in the nickel and lead concentration is successfully achieved by metering alkali sulphide into the (saturated) iron(II) salt solution (roughly 8.5% by weight Fe) following preliminary neutralisation, preferably with dolomite powder, i.e. still in the acidic range at about pH 3. In a typical set-up, an iron solution (16 m^3 batch) pre-neutralised with limestone powder is drained into a tank and 100 l alkali sulphide solution (14%) are added continuously during this time. The amount of alkali sulphide to be added is determined empirically beforehand and retained. Referred solely to the total of nickel and lead, the quantity of added alkali sulphide is super-stoichiometric. However, as the jointly precipitated iron(III) ions (and partially also manganese) have to be taken into consideration, the stoichiometric surplus lies within tight limits. After addition of the sulphide, a residence time of one hour is required to complete precipitation. This is followed by filtration of the heavy-metal sulphides, along with the heavy-metal hydroxides, which can be effectively performed using a membrane filter press. The filtrate from the filter press of the now purified iron(II) chloride

solution contains nickel and lead in concentrations that satisfy the requirements prescribed by law.

One major advantage of this method is that the very good filterability of "spherical" hydroxides, as illustrated in DE 42 43 559 A1, is not impaired by sulphide precipitation.

If NaHS in bags is used as the starting material, the occurrence of an odour nuisance due to hydrogen sulphide during preparation of the alkali sulphide solution is more likely than when using Na_2S in bags.

The results are presented in detail in Table 1. As the purification effect is comparably good in both cases, the plant trials speak in favour of the use of Na_2S flakes.

Table 1

Solution of:	NaHS	Na_2S
Quantity added per 200 t batch	11.6 kg (equivalent to 600 ppm NaHS, 70 - 72%)	20 kg (equivalent to 1000 ppm Na_2S, 60 - 62%)
Mean sulphide ion content [ppm]	240	246
Ni content of starting samples [mg/mol Fe]	35 - 50	
Pb content of starting samples [mg/mol Fe]	6.6 - 8.4	
Mean Ni content after elimination [mg/mol Fe]	16	7.5
Mean Pb content after elimination [mg/mol Fe]	4.9	4.7

Patent Claims

1. Method for eliminating nickel and lead ions from iron(II) salt solutions by precipitating and separating the corresponding sulphides, characterised in that an alkali sulphide is added at a super-stoichiometric rate in the acidic range and the precipitate is filtered off after a residence time.

2. Method according to Claim 1, characterised in that the iron(II) salt solution is obtained by leaching the cyclone dust occurring in the manufacture of titanium dioxide by the chloride process.

3. Method according to Claim 1, characterised in that the iron(II) salt solution is a steel-pickling solution.

4. Method according to one of Claims 1 to 3, characterised in that the pH range of the iron(II) salt solution during addition of the alkali sulphide is between 3 and 3.5.

5. Method according to one or more of Claims 1 to 4, characterised in that sodium hydrogensulphide is added as the alkali sulphide.

6. Method according to one or more of Claims 1 to 4, characterised in that sodium sulphide is added as the alkali sulphide.

7. Method according to one or more of Claims 1 to 6, characterised in that the alkali sulphide is added in the form of an aqueous solution.

8. Method according to one or more of Claims 1 to 7, characterised in that the quantity of alkali sulphide added for a saturated iron(II) solution is in the range of 600 to 1000 ppm.

9. Method according to one or more of Claims 1 to 8, characterised in that the residence time up to separation of the sulphide precipitate is in the range of 1 hour.

10. Method according to one or more of Claims 1 to 9, characterised in that the residual nickel content after sulphide precipitation is below 30 mg per litre iron salt solution.

11. Method according to one or more of Claims 1 to 9, characterised in that the residual lead content after sulphide precipitation is below 7.5 mg per litre iron salt solution.